Long-term monitoring of cloud chemical composition in the UK and implications for estimating wet deposition.

J N Cape, R I Smith, D Fowler,

CEH Edinburgh

K Beswick, T Choularton

University of Manchester

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EXECUTIVE SUMMARY

- Continuous monitoring of rain and cloud water amount and composition has been conducted at Holme Moss (southern Pennines) since 1994.
- Year-to-year variation in rain and cloud amount has been large, but with no temporal trend.
- Wind speed at Holme Moss has increased over the period, especially from the prevailing SW wind direction. The effect on transporting pollutants to the site is not known.
- Concentrations of non-marine sulphate in rain and cloud have decreased significantly over the period, consistent with the large decrease in UK emissions of sulphur dioxide. Concentrations of nitrate in rain and cloud have decreased slightly, not matching changes in NOx emissions in the UK, as noted for other sites in the UK rainfall network. Ammonium concentrations show no significant temporal trend. There is no temporal trend in sea-salt concentrations.
- Deposition of ions follows similar temporal trends to concentrations.
- There were no temporal trends in the ratio of cloud to rain water concentrations of ions at Holme Moss, nor in the 'scavenging factor' used to calculate seeder-feeder enhancement of deposition.
- The average scavenging factor for sea-salts of 3.6 was higher than the default value of 2 used across the whole UK for modelling seeder-feeder enhancement of all ions. Average scavenging factors for other ions were all less than 2.
- Scavenging factors of 2 or less are related to the presence of gas-phase components of sulphate, nitrate and ammonium which are not included in the seeder-feeder model, and/or to local sources that affect only one of a pair of monitoring sites.
- Uncertainties in the use of the seeder-feeder model are shown to be within the year-to-year variability for modelled total deposition across the UK as a whole. Uncertainties in Critical Load exceedance are also small for a Critical Load of deposited nitrogen of 10 kg ha^{-1} y^{-1} which is typical of many upland areas, but could be large for areas with higher Critical Loads if they occurred in areas where seeder-feeder enhancement is an important component of total deposition.
- The results point to deficiencies in our knowledge of the spatial variation of the scavenging factor for different ions across the UK, and in the variation of trace gas concentrations with elevation.
- Options are provided for the extension, continuation or cessation of this monitoring work, with the associated pros, cons and approximate cost implications.
- Recommendations include: stopping cloud water monitoring, monitoring of additional paired high- and low-elevation sites for rainfall composition, and installation of (conditional) trace gas and particle integrating samplers at paired high- and low-elevation sites for a restricted period.

Contents

1. Introduction

Routine measurements of cloud composition and rainfall composition at high elevation were started in 1993, following a series of intensive field campaigns at Great Dun Fell in the northern Pennines, which showed that not only rainfall amount but also rain composition increased with altitude, leading to much greater wet deposition of pollutants on western hills than had been expected (Choularton, et al., 1988, Fowler, et al., 1988). The intensive field campaign measurements also demonstrated the mechanism for these increases, in terms of the 'seeder-feeder' effect (Figure 1). As rain from high-level clouds falls through the atmosphere to low elevation sites, it does not effectively scavenge the fine (sub-micron) aerosols in the atmosphere, so that rain composition measured at low levels reflects the composition of the high level precipitating cloud. However, as surface air is lifted over a range of hills or mountains, it is cooled, permitting condensation of water vapour on the aerosol particles, which act as cloud condensation nuclei, forming cloud droplets that may be hundreds of microns in diameter. The hill cap cloud formed in this way has a different chemical composition from the precipitating high-level cloud (which may have formed over the ocean); the cap cloud composition reflects the composition of the inflowing surface air, which may contain a range of pollutants in both gas and particulate form. As the falling rain from the upper cloud passes through the hill cap cloud, the cloud droplets (now much larger than the original aerosol particles) are efficiently scavenged, leading to increased amounts of water deposited, as well as deposition of the material present in the inflowing air.

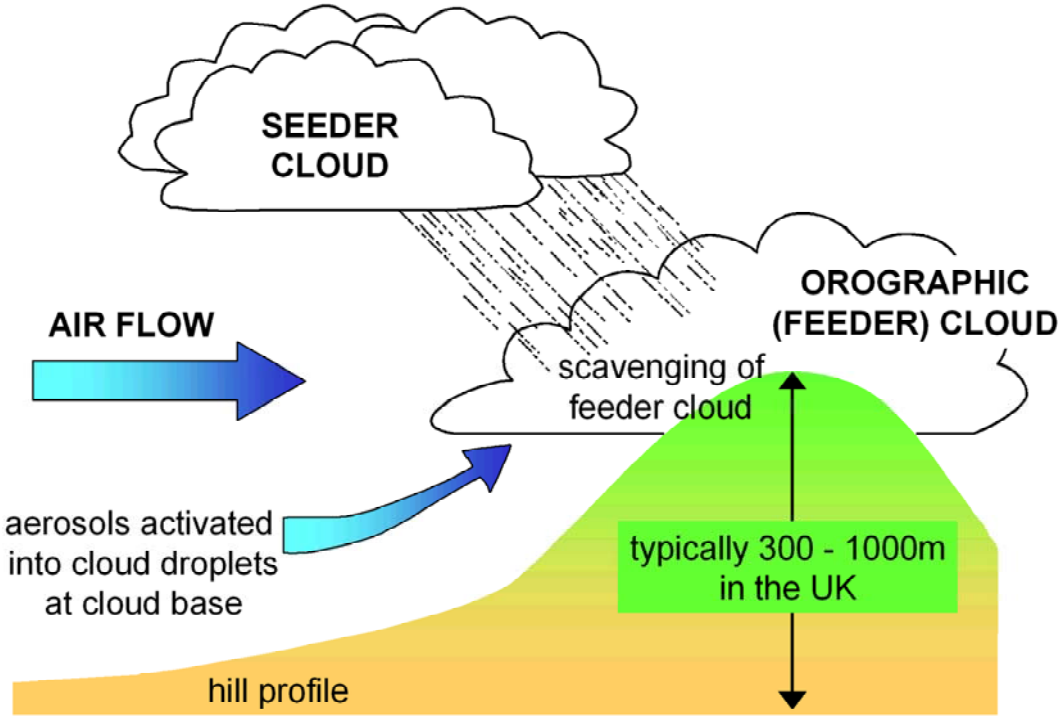

Figure 1. Schematic of the seeder-feeder process. Falling rain upwind of the hill cloud does not scavenge efficiently particles from the atmosphere. Once they are activated into cloud droplets in the cap cloud, particles are scavenged efficiently and deposited under the cap cloud, which also contributes additional water to deposition at the hill summit.

Subsequent field campaigns elsewhere in the UK (Snowdon, N W Scotland, central Scotland) (Fowler, et al., 1995, Inglis, et al., 1995) showed that such 'seeder-feeder' enhancement occurred wherever an orographic cap cloud formed – and the process was successfully modelled by researchers at UMIST (now University of Manchester) (Dore and Choularton, 1992). The challenge was to use this information to estimate the deposition of acidifying and

eutrophying pollutants in all upland areas of the UK, in order to quantify deposition for comparison with Critical Loads, and in order to calculate a budget for the UK. The field campaigns showed that the average concentration of many ions in the scavenged cloud was approximately twice that in the low-level rain measured nearby – this factor of 2 as a 'scavenging factor' has been used routinely for modelling wet deposition to upland areas (see below). Moreover, the measurements of cloud composition on hill tops showed that concentrations were very much greater than in rain, depending on the proximity of the sampling site to cloud base, where droplets were smallest and concentrations largest. It was recognised that direct capture (by turbulent deposition) of cloud droplets by upland vegetation would therefore comprise an important contribution to total deposition; the cloud:rain concentration factor for modelling direct cloud water deposition (in the absence of rain) was empirically established as a factor of 5.

The long-term measurements at Holme Moss (and at Dunslair Heights – see below) were established to provide a check on the continuing validity of these parameterisations over time, given that trends in emissions of sulphur and nitrogen-containing pollutants were likely to lead to significant changes in air composition.

The method for mapping the seeder-feeder enhancement of wet deposition across the UK is illustrated in Figure 2. From the UKEAP monitoring network, the average annual concentration of ions is established (by kriging or interpolation) across the country, using the data from the low-level monitoring sites. The amounts of rainfall are similarly established for low elevations at the west and east coast, using modelled data at 5 km resolution from the Meteorological Office. For an upland area in the centre of the UK the expected 'low-level' rainfall quantity and concentration are calculated based on the interpolated/modelled data. The additional rainfall amount predicted for the high elevation is then taken to represent the volume of cloud water scavenged at the high elevation, and the concentration of this scavenged cloud water is set as twice the expected concentration for low-level rain at the site (i.e. the scavenging factor is taken as a factor of 2). The total additional wet deposition at the high elevation is then calculated as the product of the additional scavenged cloud water and its concentration, added to the predicted low-level deposition at that geographical location.

This method of calculation is used for all the maps of wet deposition used in the UK for Critical Load assessments, and drives the exceedance of Critical Loads in many upland areas of the UK, but has little influence on wet deposition in lower-lying areas, and consequently on the overall UK deposition budget. Sensitivity to different values of the scavenging factor is discussed below (Section 5).

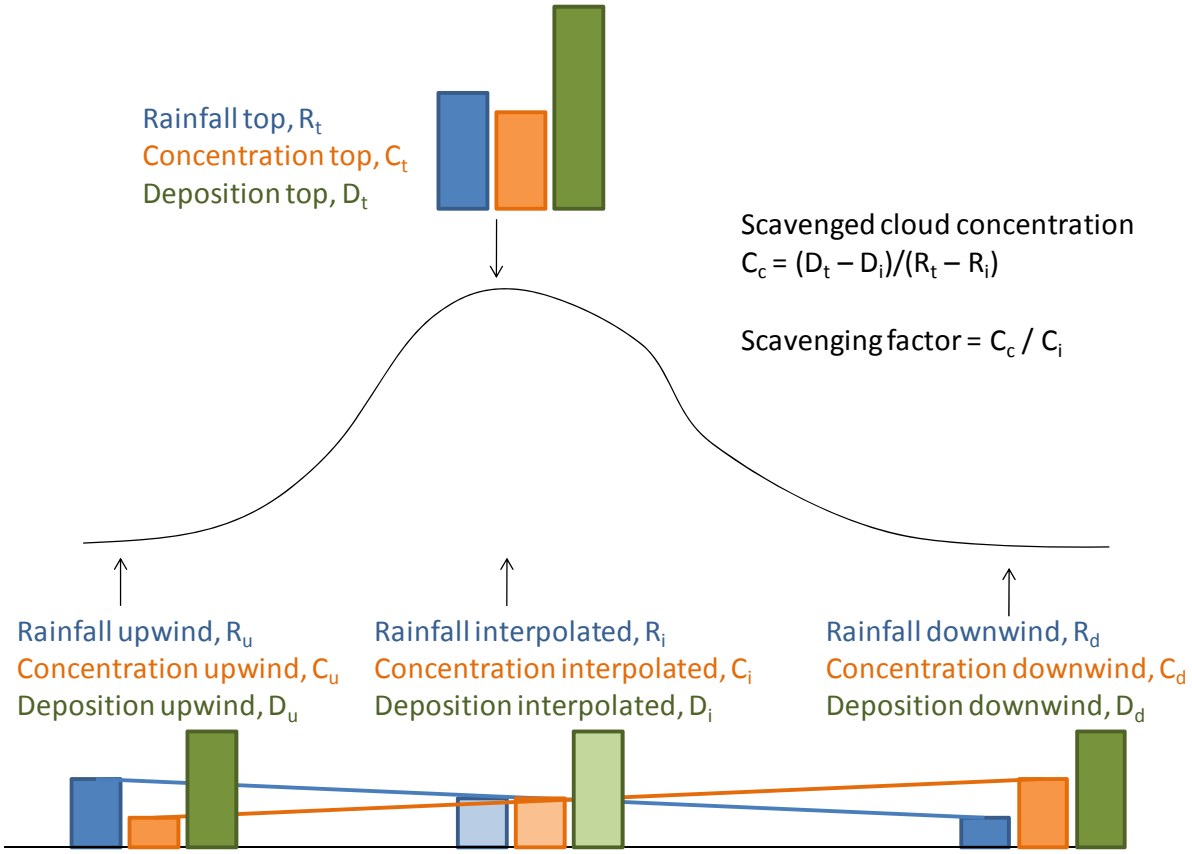

Figure 2. Schematic of the mapping process for calculating orographic enhancement of wet deposition across the UK. The amount of scavenged rain (water) is calculated as $R_t - R_i$, where R_i is interpolated from rainfall at low-elevation sites upwind and downwind, and R_t is measured or modelled based on altitude and location. The additional ion deposition is given by $(R_t.C_t)-(R_i.C_i)$, where the vertically integrated cap-cloud concentration (C_c) for a scavenging factor of 2 is $2C_i$, C_i is interpolated from the low-elevation sites upwind and downwind, and $C_c = (R_t.C_t - R_i.C_i)/(R_t - R_i)$, i.e. $C_t = C_i.(2 - R_i/R_t)$.

2. Long-term cloud monitoring in the UK

Two sites were established for long-term monitoring, each equipped with a suite of collectors. One was at Holme Moss, 35km ENE of the Manchester conurbation (lat. 53.532N, lon. -1.857E, elevation 525m), for which the linked low-level site in the UKEAP network is at Wardlow Hay Cop (lat. 53.260N, lon. -1.735E, elevation 300 m). The other was at Dunslair Heights in the Scottish Borders, with a linked low-level site at Venlaw. At each high-level site a standard bulk rain collector was established, along with a 'harp-wire' cloud collector (Figure 3). At Dunslair an additional 'lidded' cloud collector was established, from which incident rain was excluded, at least at moderate wind speeds. Additional meteorological instruments provided information on wind speed and direction, rain and cloud water amount (by tipping bucket rain gauge). The site at Dunslair became unsuitable as a long-term monitoring site because the growth of the adjacent forest led to sheltering of the hill top where the samplers were located, and decreasing capture of hill cloud. The site was moved in 2003 to a neighbouring hill (Bowbeat) at the same elevation, only 4 km to the north, and the low-level site was relocated to Auchencorth Moss. However, subsequent operation of the sites showed little seeder-feeder enhancement at the Bowbeat site relative to

Auchencorth, and sampling was abandoned in 2007. This review of long-term trends in rain and cloud composition therefore is based on an analysis of the data from Holme Moss and Wardlow Hay Cop only.

Figure 3. Passive cloud water collector at Holme Moss

The measurements at Holme Moss up to 2001 have already been described (Beswick, et al., 2003). This review showed decreasing sulphate concentrations and deposition, and increasing amounts of cloud water over the 8 years. The current analysis takes the period up to the end of 2008, and examines temporal trends in composition and deposition at both sites (Holme Moss and Wardlow Hay Cop), trends in cloud composition, and in scavenging factors derived from the seeder-feeder analysis. On the basis of the trends in UK emissions since 1994, we might expect to see a large decrease in concentration and deposition of sulphate, a smaller decrease in nitrate, a much smaller decrease in ammonium, and no significant change in sea salts (sodium, chloride, magnesium). We also wish to examine whether there has been a trend in the scavenging factors of any ions, and whether the default factor of 2 used in the mapping method is still valid. For direct cloud water deposition to upland vegetation, we also need to establish whether there has been any trend in the relative concentration of cloud and rain water, and whether a factor of 5 is still appropriate for modelling deposition in cloud water.

3. Results from measurements

3.1 Rain and cloud water amounts

The amount of rain and cloud collected will have consequences for the concentrations of ions in the samples averaged over long periods. In general, the more rain is sampled, the more dilute the samples are likely to be to be; raindrops will on average have passed through a greater thickness of cloud, thereby enhancing their volume, but scavenging larger and more dilute cloud droplets. For years with a higher cloud amount, it is expected that the summit of Holme Moss would on average be in a part of the cloud with larger droplets, and will therefore once again yield more dilute samples.

Bulk rainfall amount from November 2007 onwards has been corrected following the installation of a new collector. Although the replacement collector was very similar to the original, there was a substantial decrease in the collection efficiency when compared to the standard tipping bucket rain gauge used at the site. It appears that the sampler may move from the vertical over time, leading to systematic under-sampling of rainfall amount, but re-alignment of the sampler on several occasions through the period means that this should have no great effect on long-term trends, but may add to the intra-year variability. Rainfall amounts used for deposition calculations are derived by comparison of the actual amount sampled for chemical analysis with the data from the tipping-bucket collector at ground level.

The cloud samples are contaminated by rainfall, with the cloud collectors sampling 90-95% of the rain volume collected by the rain sampler. Sample volumes have been corrected for this additional rainfall.

The data in Figure 4 show that the difference in recorded precipitation amount between Wardlow Hay Cop and Holme Moss varies greatly from year to year, and is not directly related to the amount of cloud water sampled at Holme Moss. The difference in precipitation amount reflects the average depth and water content of the cap cloud scavenged by falling rain, whereas the cloud volume collected reflects the water content and amount (frequency) of cloud at the sampling site. For example, in 2004 although the amount of additional precipitation recorded at Holme Moss was relatively small, the amount of cloud water collected was large, implying greater frequency and water content of cloud at Holme Moss in 2004 despite the lack of rainfall.

Over the period there was no obvious trend in rain or cloud amount at either site. The apparent trend from 1994 to 2001 (Beswick, et al., 2003) was not sustained in subsequent years. The ‘enhancement factor’, i.e. the ratio of rain amount at Holme Moss relative to Wardlow Hay Cop, also showed no overall trend, with an average over the 15 years of 2.9 (±0.9).

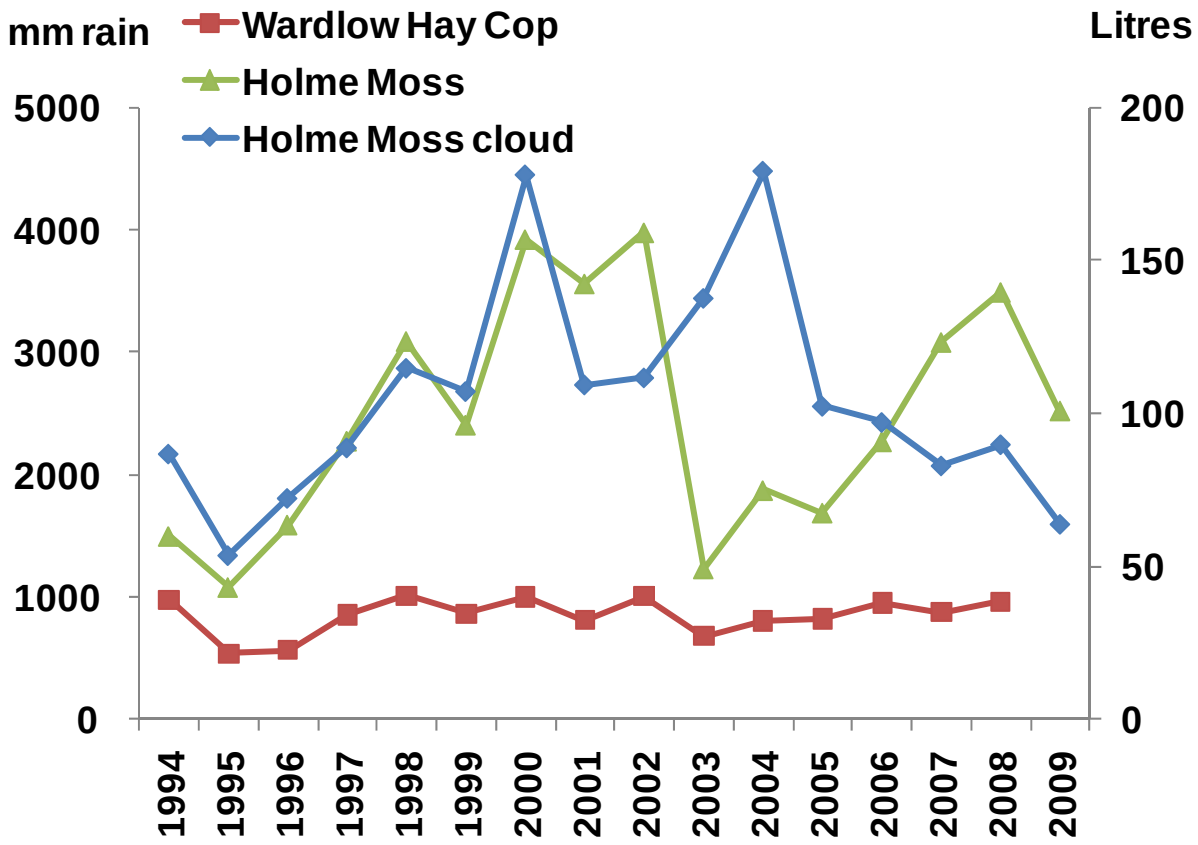

Figure 4. Rainfall amount measured at Wardlow Hay Cop and Holme Moss (LH axis), and volume of cloud water sampled at Holme Moss (RH axis), corrected for rainfall sampled by the cloud collector.

3.2 Application of quality-control measures (dataset matching)

In order to compare the chemical composition of rain and cloud water at the two sites, rigorous quality control measures are needed to avoid the inclusion of samples which have been contaminated. Data from the UK secondary network (now UKEAP) site at Wardlow Hay Cop were retrieved from the archive (www.airquality.co.uk) and checked for consistency, especially with respect to potential contamination as evidenced by concentrations of potassium, which is associated with bird droppings. Samples with very small volumes (< 100 mL) were also discounted. Similar procedures were applied to the rain and cloud composition data measured at the University of Manchester, including comparison of ion balances and measured vs. theoretical conductivity. Periods where the amount of sample from the cloud collector was less than that in the rain collector were also excluded. These quality control measures led to reduced data coverage, but reduced the risk of contaminated samples upsetting the subsequent data analysis. Because of the requirement to compare like with like, periods for which data were not available (or excluded) at either of the sites were removed from the datasets prior to statistical analysis and calculation of relative concentrations and deposition. The effects of the quality control measures are seen in Table 1, which shows for each year the % of the measured rain or cloud volume sampled that was included in the subsequent analysis. With the exception of 1995, removal of contaminated samples made only a small difference to the overall volume of precipitation or cloud water used in the analysis below.

Table 1: percentage by volume of valid simultaneous samples in each year in rain and cloud at Holme Moss and in rain at Wardlow Hay Cop.

Year	Holme Moss rain	Holme Moss cloud	Wardlow Hay Cop rain
1994	83%	83%	79%
1995	48%	61%	56%
1996	85%	77%	86%
1997	95%	93%	95%
1998	95%	92%	94%
1999	96%	94%	97%
2000	90%	83%	99%
2001	94%	95%	100%
2002	81%	81%	84%
2003	88%	85%	90%
2004	86%	91%	95%
2005	96%	94%	96%
2006	89%	87%	91%
2007	91%	94%	100%
2008	78%	84%	90%

3.3 Trends in wind direction, climate etc.

The concentration of ions in individual samples depends on the source of the air flowing over Holme Moss, with some directions expected to be associated with higher levels of pollutants as a result of the geographical location of major pollutant sources such as heavy industry and power generation. Over longer periods, the volume-averaged concentrations will be heavily influenced by the prevailing wind direction.

At Holme Moss, the prevailing wind direction is from the south-west quadrant, whilst the highest pollutant concentrations can be found in the north-east quadrant. There is some evidence to show that between the periods 1996-9 and 2006-9 there was a shift towards a greater proportion of the air arriving at Holme Moss having come from the prevailing direction, increasing from 55 to 65% of all 1 hour data (Figure 5). There is also a narrowing and shifting of the north-eastern lobe of the wind direction frequency. There is potential for these changes to have an effect on the ion concentrations, although the effect may be small.

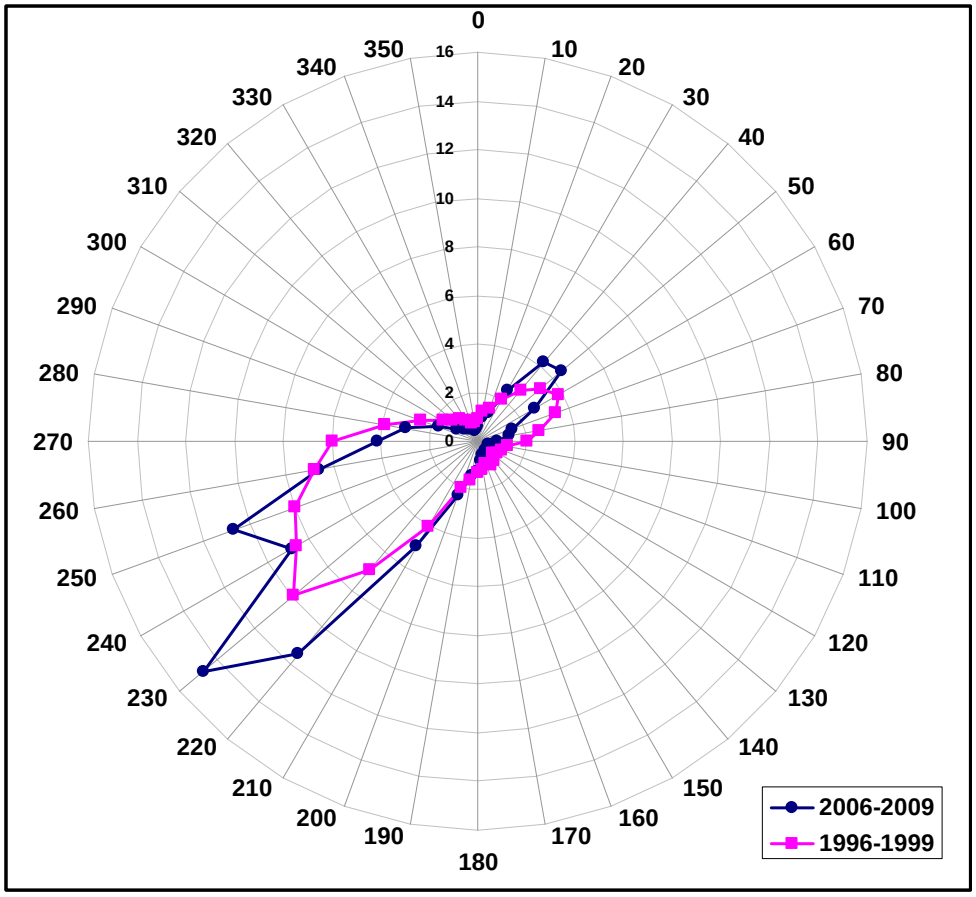

Figure 5. Average pattern of wind direction at Holme Moss between 1996 and 1999 and between 2006 and 2009, showing small changes in the source of air at the site.

It should be noted that when analysing the wind direction distribution of ion concentrations, sectors of 22.5 degrees are used, due to the much reduced number of samples available: bulk collections for chemical analysis are taken weekly, whilst the wind direction rose shown above is calculated using hourly data from the automatic weather station. Additionally, since the bulk samples are taken over a longer period, it is common for the weather conditions to change significantly during the sampling period. To ensure that the wind direction calculated for the bulk collections is representative of the conditions that produced the largest volume of rain and cloud collection, only wind data during wet periods of the sample are used. One consequence of this is that the wind direction distributions of ion concentrations are not necessarily directly comparable with the wind roses for wind speed, wind direction frequency and the PWS data (see below), which cover all measured valid wind data.

There are clear maxima in the distribution of wind speed as a function of wind direction (Figure 6). There is a major peak in the S to W sector, and a secondary peak in the NNE to E sector. These peaks have become noticeably better defined over the measurement period, with peak wind speeds increasing significantly from 6 to 9 m s^{-1} (Figure 7). Along with the shift in wind direction frequency distribution, there is reason to believe that there has been a change in prevailing conditions at the site, with consequent effects on the ion concentrations observed. Note that there were insufficient wind speed data from 2005 and 2006 to enable these years to be used in comparisons.

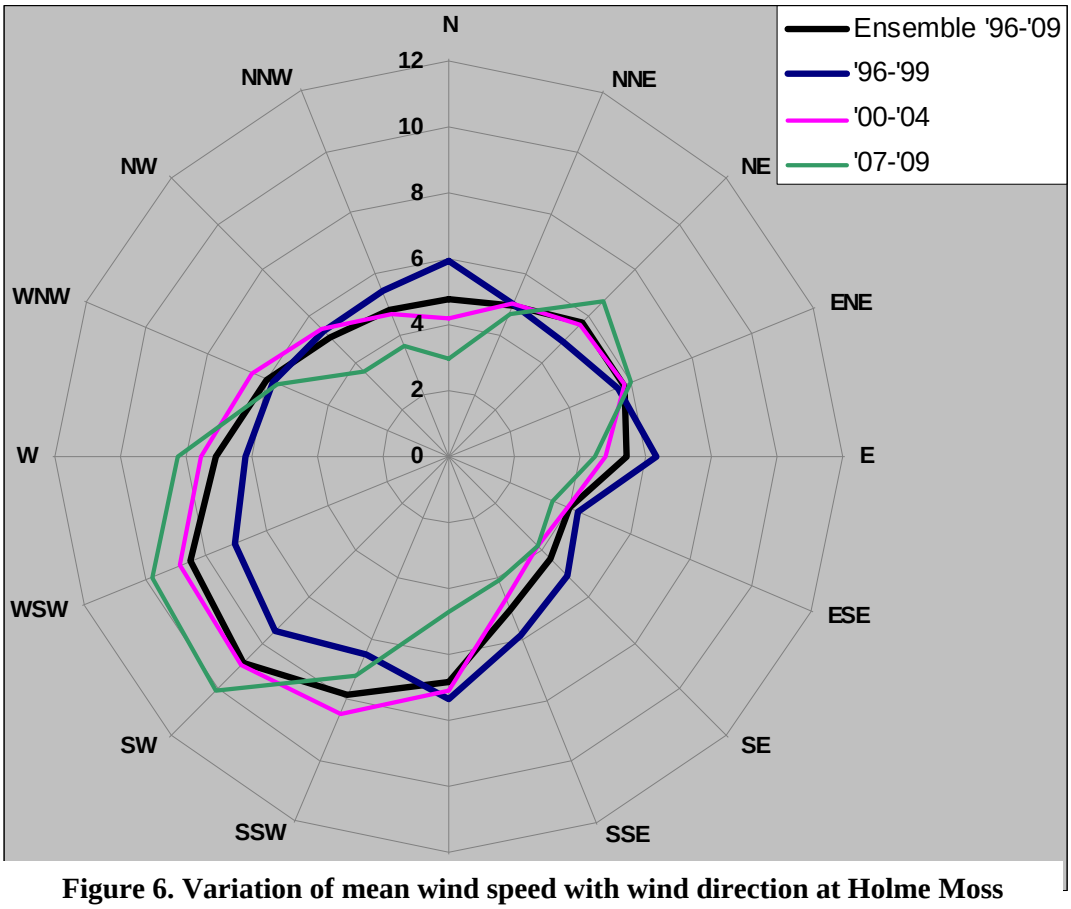

Figure 6. Variation of mean wind speed with wind direction at Holme Moss during three periods: 1996-99, 2000-04, 2007-09

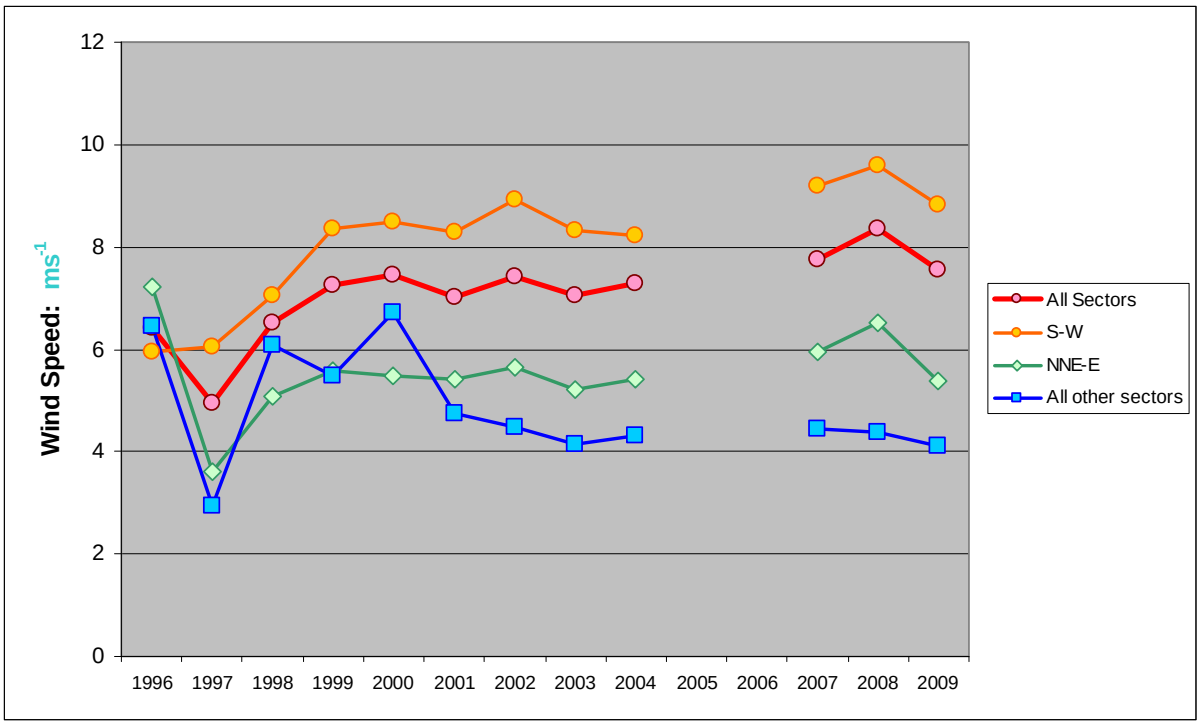

Figure 7. Long-term trends in mean wind speeds at Holme Moss as a function of wind direction

Holme Moss also has data available from a Present Weather Sensor (PWS) for a number of the years in which rain and cloud sampling has taken place. Reliable data are available for 1999-2002, 2004 and 2008-9. These data are collected every minute, and give an indication of precipitation, precipitation type and intensity, cloud presence and visibility. The data are normally averaged over hourly periods to match data from the AWS. Analysis of the data reveals trends which may affect the interpretation of the ion concentration data.

In common with the wind speed data, the PWS data indicate a general narrowing of the wind directions in which cloud and rain are experienced. There is a trend for the site to spend more time in cloud in the NNE-E sector and less time in the S to W sector, with time spent in the NNE-E sector being 2-3 times that spent in the S-W sector. In contrast, the bulk collectors show most cloud to be collected in the SSW-W sector, with a secondary peak in the NE-E sector. This may indicate three things: firstly, the PWS analysis uses all available data, whereas the bulk samples are limited to significant wet periods only; the collection efficiency of the cloud collector may be wind speed dependent, with the wind speed in the SW being approximately 1.5 times that in the NW - this may distort the volume collected as a function of wind direction; the PWS indicates cloud whenever the visibility drops below 100m - it is unlikely that the bulk collector is efficiently collecting cloud this thin, thus the PWS whilst accurately indicating the presence of cloud, may not give a sample duration directly equivalent to the bulk collector (Figure 8).

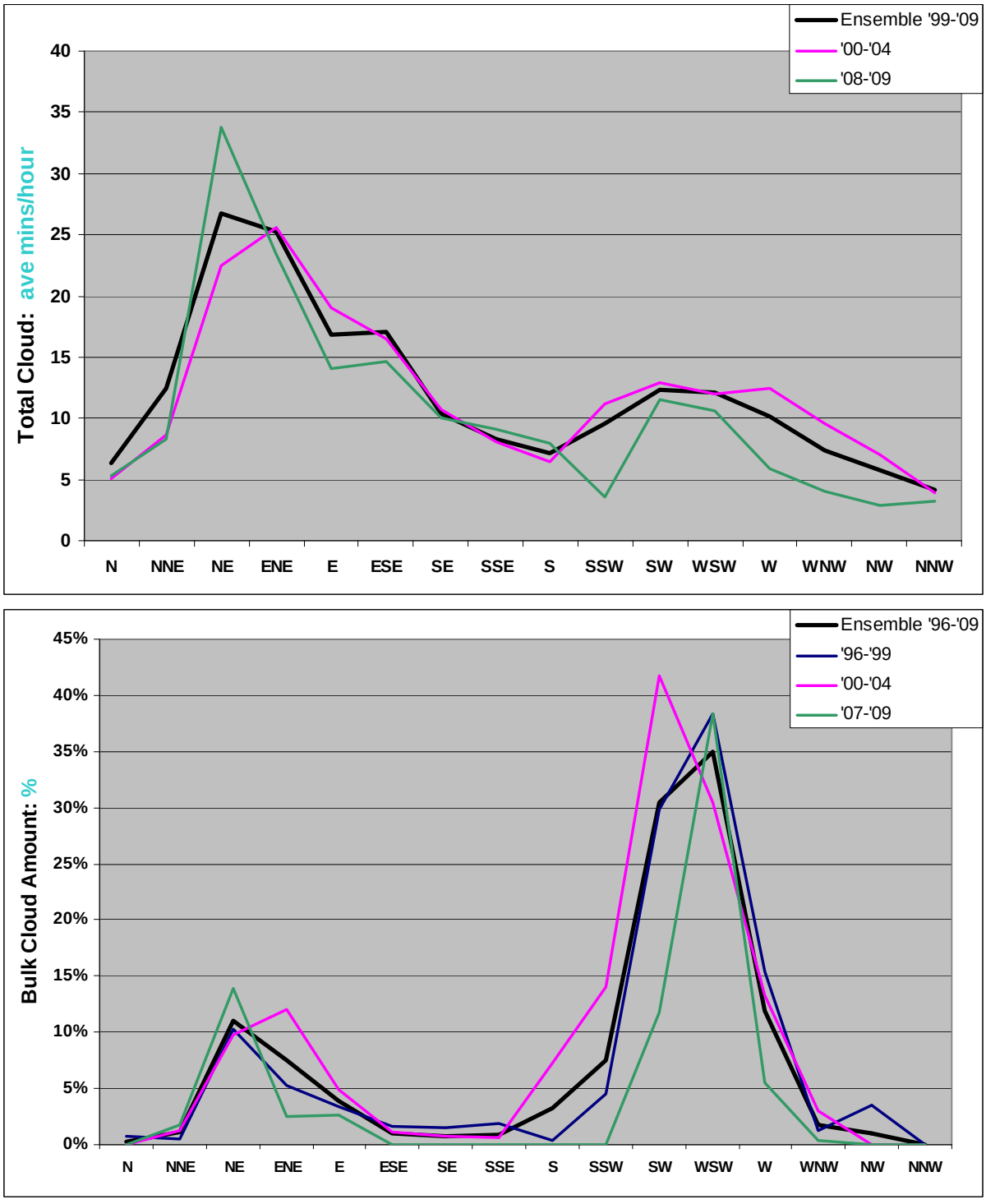

Figure 8. Comparison of wind directional distribution during cloud from the Present Weather Sensor, based on visibility (upper), and Automatic Weather Station data (lower).

For rain, there is better agreement between the PWS and the bulk collectors, both seeing a primary peak in the S to W sector, although the PWS distribution is far broader, probably as a result of the larger data set. The PWS sees a decrease in the amount of time experiencing rain conditions from 17 to 13 minutes per hour on average in the S-W sector (Figure 9).

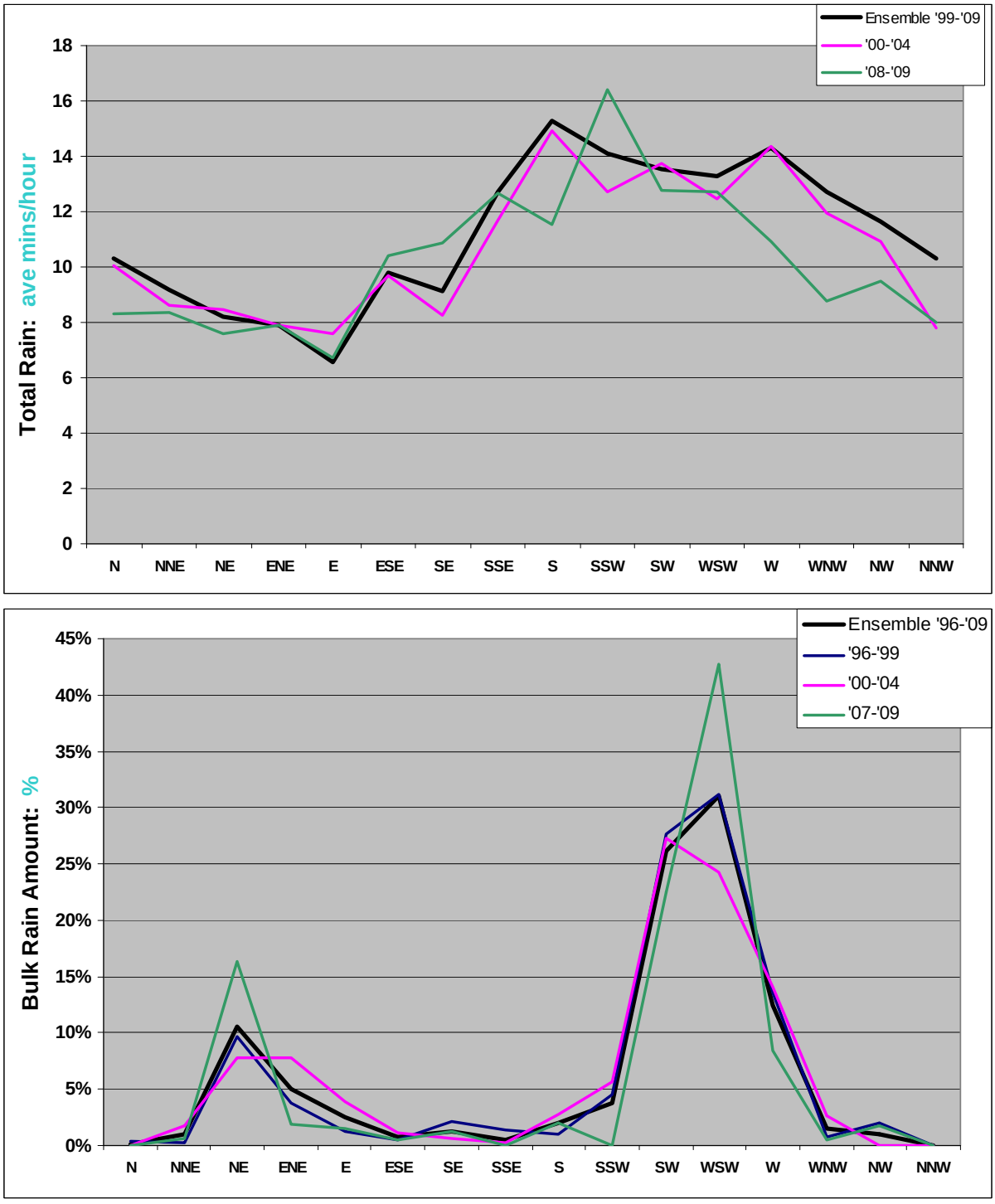

Figure 9. Comparison of wind directional distribution during rain from the Present Weather Sensor, based on precipitation (upper), and Automatic Weather Station data (lower).

3.4 Trends in rainfall composition (high level and low level)

The trends in concentration in rain at Wardlow Hay Cop and Holme Moss are shown as the annual rainfall-weighted concentrations for each of the major ions in Figure 10. These data are derived from the quality-controlled data set and are matched between the two sites to avoid any bias caused by omitting a sampling period from one site and not the other. The sampling periods do not match exactly, but the best estimate of temporal matching has been used in creating the quality-controlled datasets.

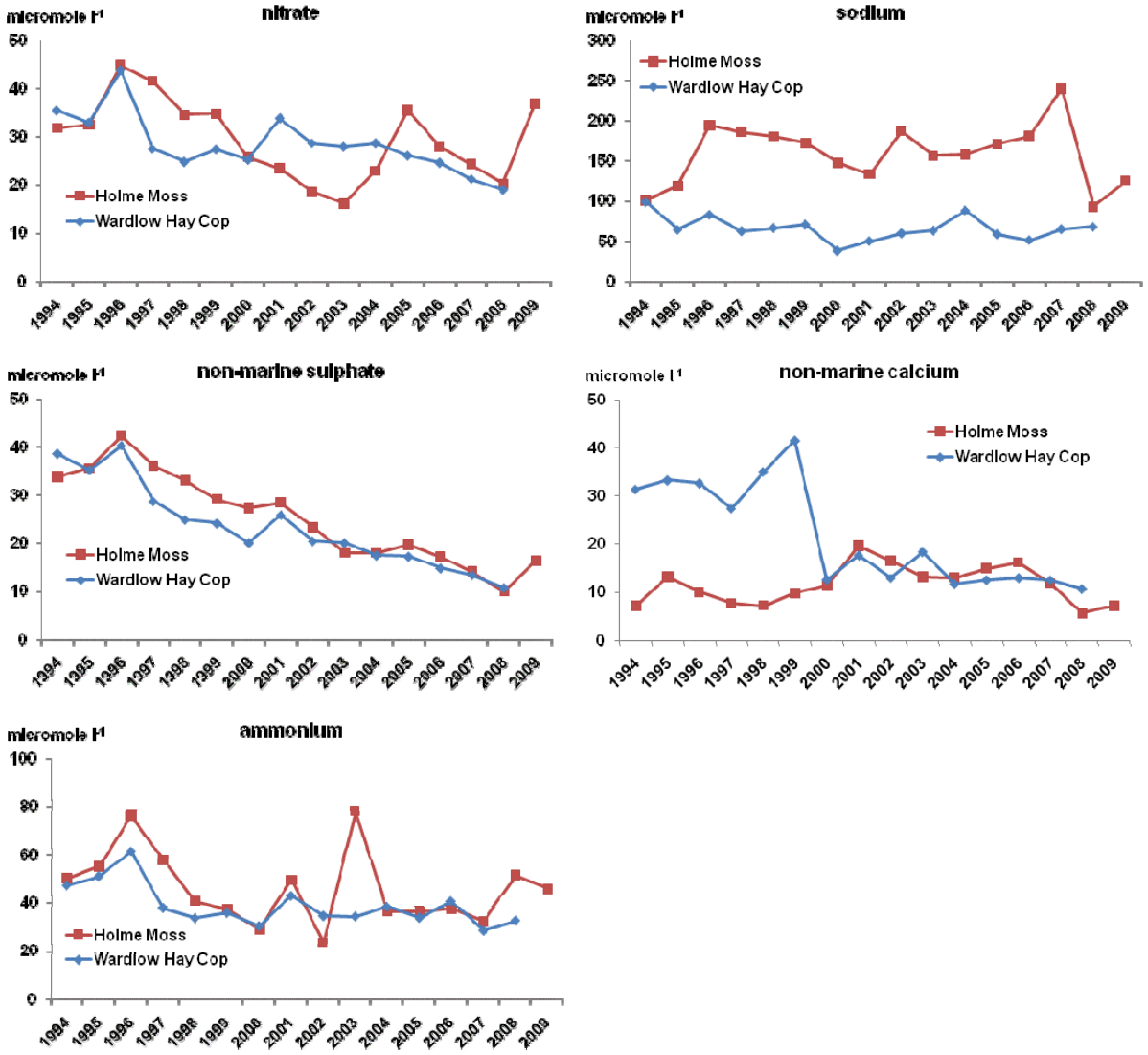

Figure 10. Trends in annual volume-weighted concentrations of major ions in rain at Holme Moss and Wardlow Hay Cop, based on matched samples

The trends depicted above show a small decline in concentrations of nitrate at both sites, with no systematic difference between the sites. By contrast, there is a marked decrease in non-marine sulphate over the period, by a factor of 4, and with concentrations on average slightly higher at Holme Moss. There is very little trend in ammonium concentrations; there is a particularly high value at Holme Moss in 2003, which was a very dry year. Concentrations at Wardlow Hay Cop are less variable from year to year and show a small downward trend. Concentrations of sodium show no strong trend, although concentrations at Holme Moss

from 1996 to 2007 were higher than the years immediately before and after. At Wardlow Hay Cop concentrations were more stable. The non-marine calcium concentrations are fairly stable at Holme Moss, but show a large step change at Wardlow Hay Cop in 2000. This large change has been seen at other sites in the UK network, and was caused by a change in analytical method for cations in the laboratory analysing the samples.

3.5 Trends in cloud composition

The annual volume-weighted concentrations in cloud water sampled at Holme Moss are compared with the concentrations in rain in Figure 11. No significant trends in cloud water concentrations are immediately obvious, with the exception of non-marine sulphate, which decreases through the period. The pattern of a decrease in concentrations of other ions before 2003-4 followed by an increase may be simply related to the volume of cloud water sampled, which showed the opposite pattern (Figure 4).

The effective air concentration of ions (derived by multiplying the cloud volume and the average cloud concentration) is shown in Figure 12. Because we do not have a measurement of the average cloud liquid water content, these numbers are proportional to the air concentration of the aerosol entering the cloud, but cannot be expressed directly as mass per unit volume (µg m^{-3}). However the time trends and year-to-year variation should follow the average air concentrations of aerosol upwind of the cap cloud. Again, the only systematic trend observed is for non-marine sulphate.

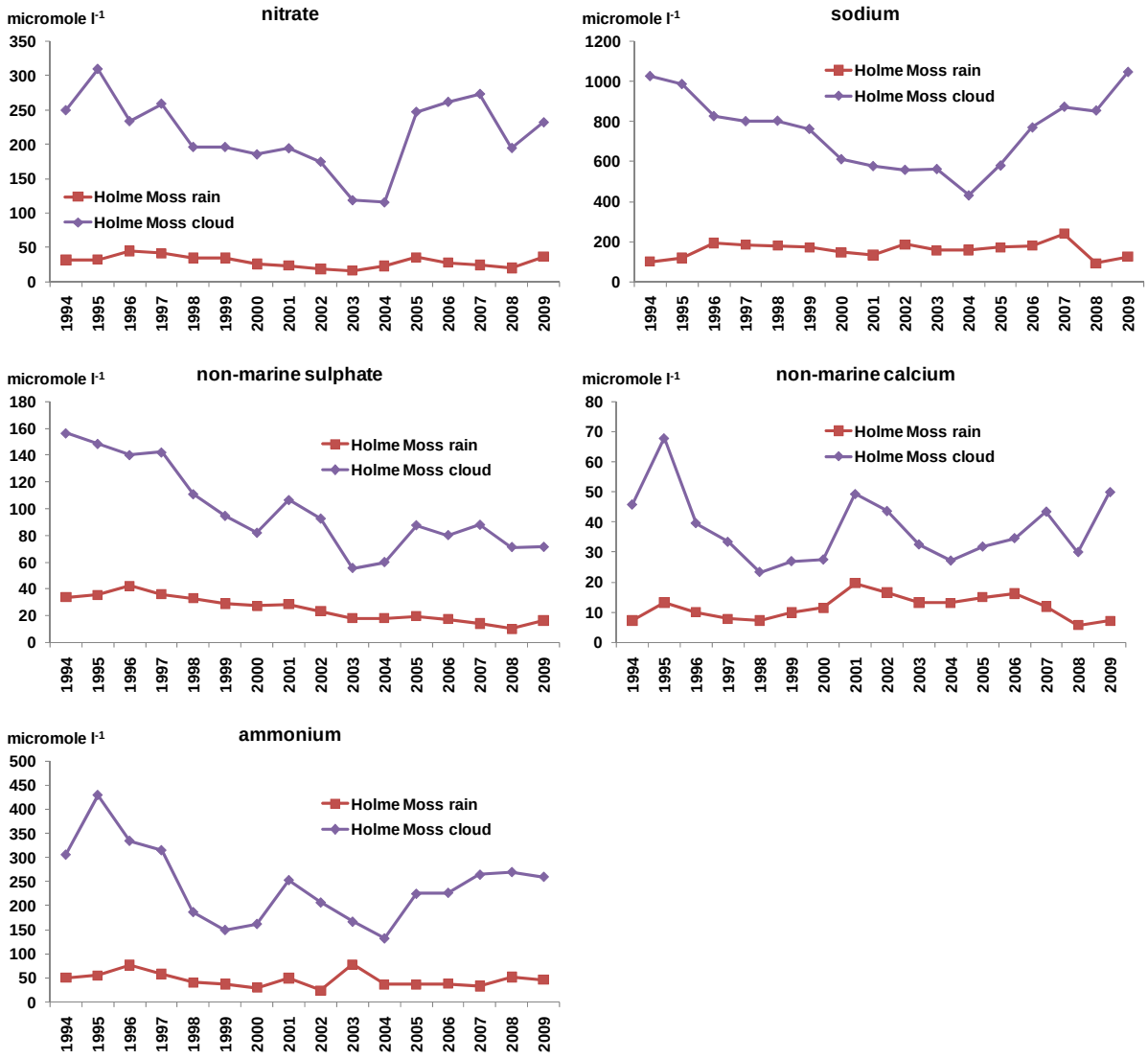

Figure 11. Trends in annual volume-weighted concentrations of major ions in cloud and rain at Holme Moss, based on matched samples

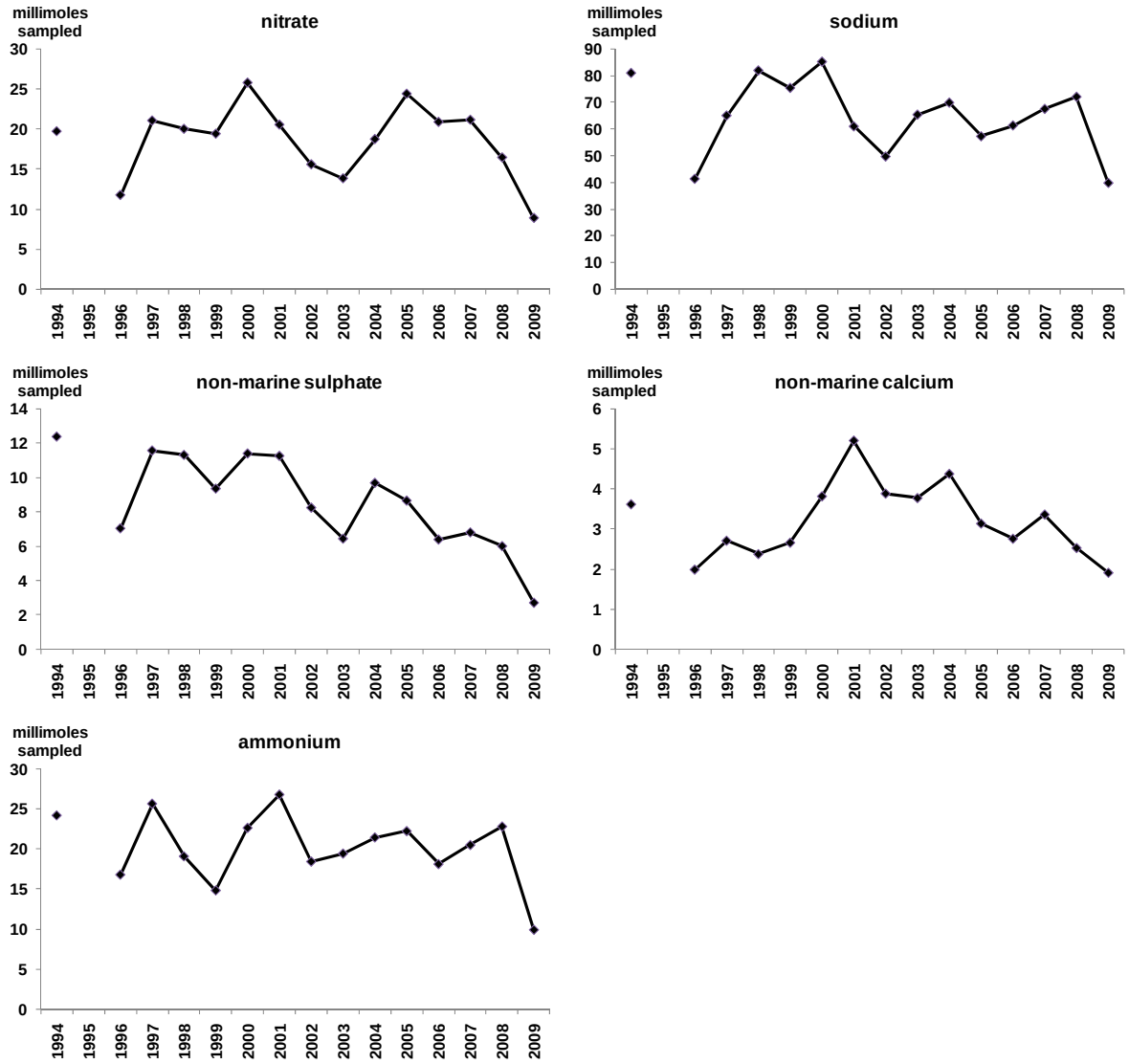

Figure 12. Amounts of ions sampled in cloud water each year (millimoles), derived by multiplying the average cloud water concentration with the volume of cloud water collected at Holme Moss. Data from 1995 have been omitted because of poor data capture (see Table 1).

3.6 Trends in cloud:rain concentration ratios

The current modelling approach for estimating the direct deposition of ions in cloud water to the surface assumes that the ratio of concentrations in cloud to concentrations in rain is a uniform factor of 5, based on earlier studies. Figure 13 shows that this is a reasonable approximation for all ions, although for some ions such as nitrate the measured ratio is somewhat greater (average 7.6) and for non-marine calcium it is somewhat lower (average 3.6). There is some variation in this ratio between years, but no clear trend over the period for any of the ions measured.

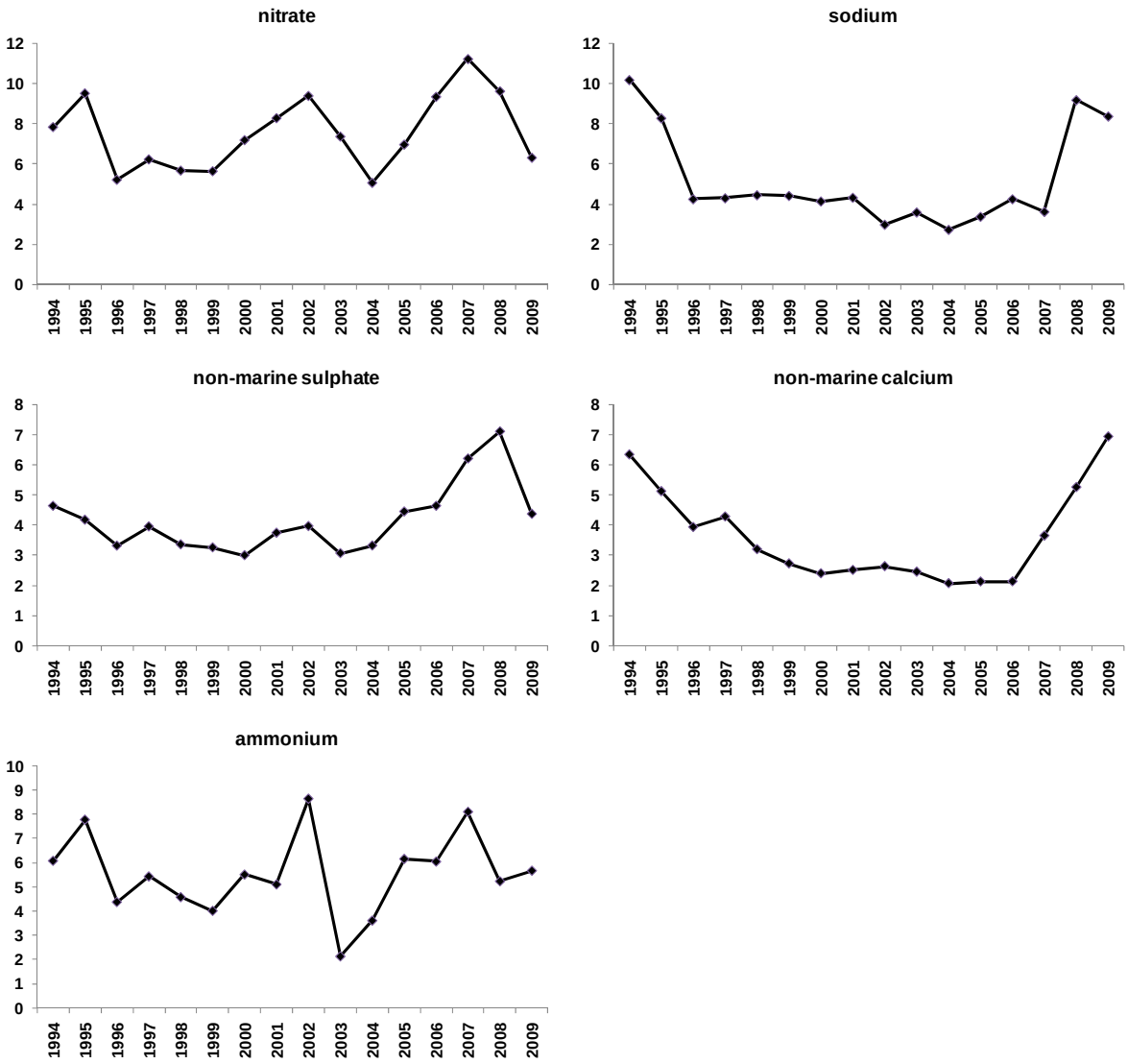

Figure 13. Ratio of average concentrations of ions in cloud water to concentrations in rain water at Holme Moss.

3.7 Trends in rainfall deposition

Long-term trends in concentration in rainfall (Figure 10) may be masked by variations in rainfall amount from year to year. The annual deposition in rain (the product of average concentration and rainfall amount) at Holme Moss and Wardlow Hay Cop is shown in Figure 14. The very dry year of 2003 (see Figure 4) is particularly obvious at Holme Moss; the data for 1995 have been omitted because of the poor data capture that year (see Table 1). The downward trends in non-marine sulphate are apparent at both sites (-5.8% yr^{-1} at Holme Moss, -7.0% yr^{-1} at Wardlow Hay Cop), but there are no significant trends in any of the other components except for a downward trend in nitrate at Wardlow Hay Cop, of -2.3% yr^{-1}. For all ions, deposition is greater at Holme Moss than at Wardlow Hay Cop (with the exception of calcium before 2000, which is related to analytical problems – see above). The difference between deposition at Holme Moss and Wardlow Hay Cop represents the additional material scavenged by falling rain from the cap cloud – the 'seeder-feeder' enhancement. The average concentration of the scavenged cloud water (Figure 15) is calculated from the difference in

deposition and the difference in the amount of rain between the two sites. The ratio of this concentration to the concentration in rain at the low-level site (Wardlow Hay Cop) is used in modelling orographic enhancement, and is referred to as the scavenging factor, or scavenging factor. Note that the concentrations of ions scavenged from cloud represent the average throughout the whole cloud depth, as opposed to the measured concentrations, which tend to be nearer cloud base, with smaller droplets, and are therefore higher.

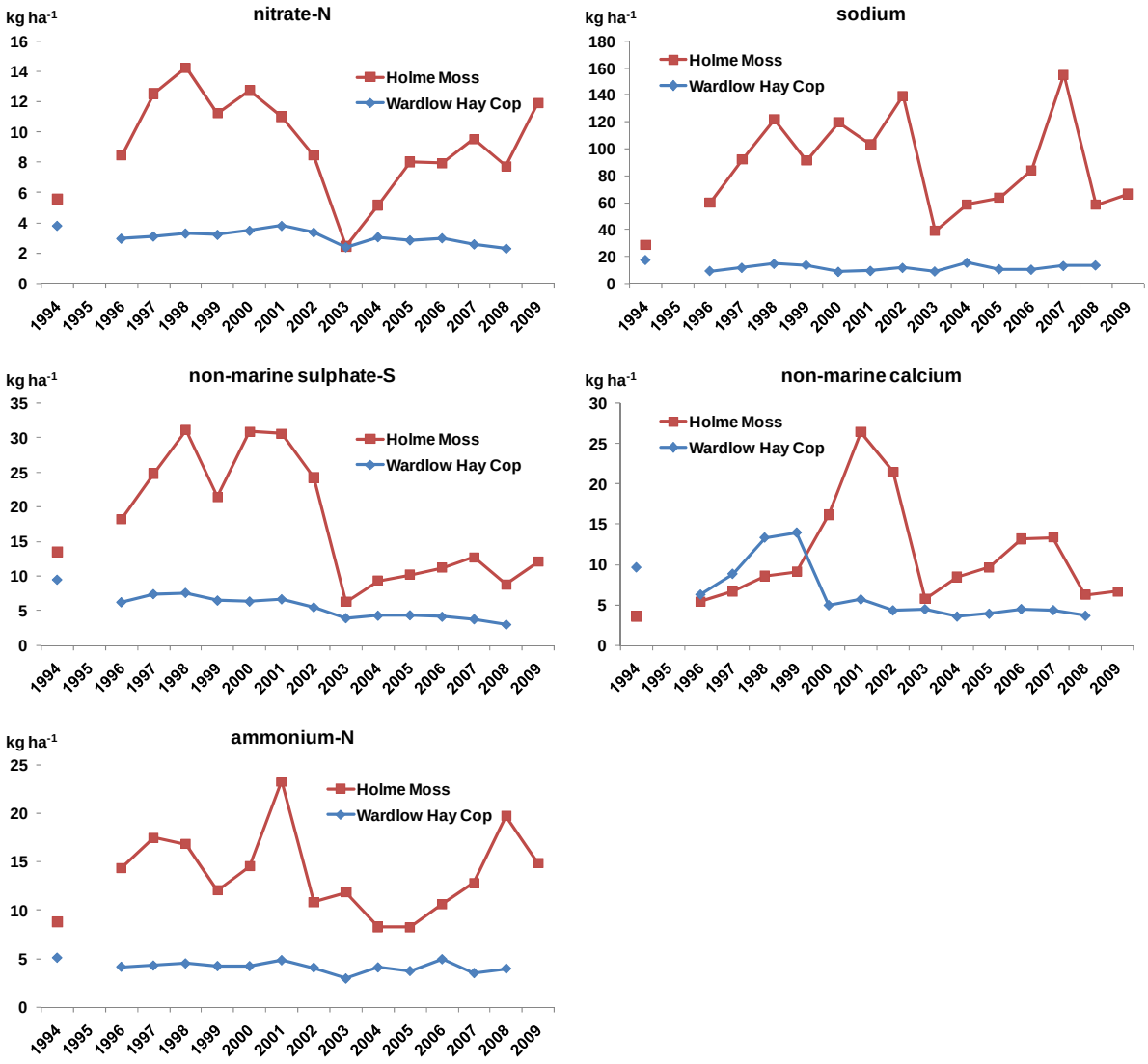

Figure 14. Wet deposition of ions in rain at Holme Moss and Wardlow Hay Cop. Data for 1995 are omitted because of poor data capture (see Table 1).

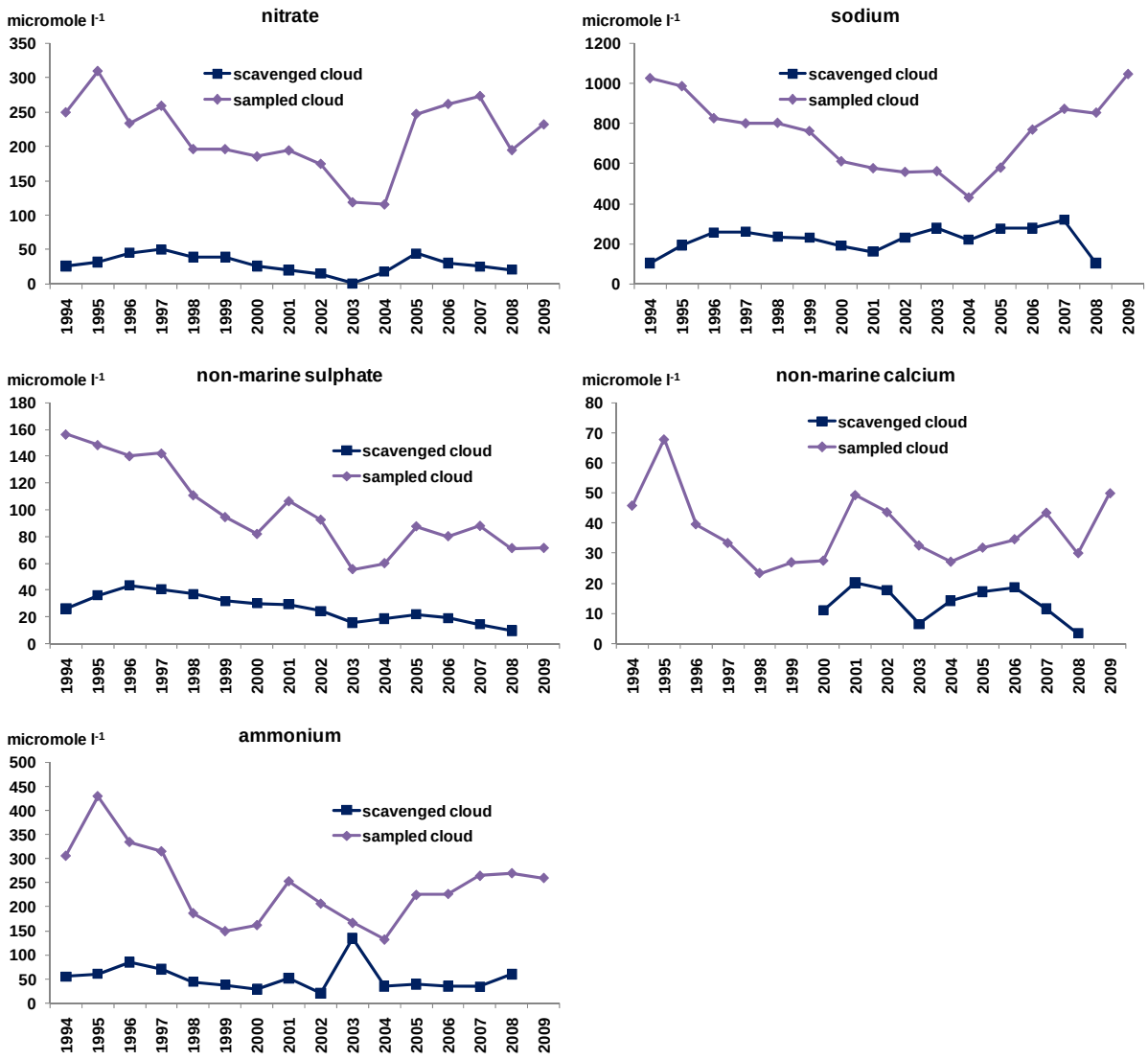

Figure 15. Concentrations of ions in scavenged cloud at Holme Moss, based on comparison with deposition at Wardlow Hay Cop. Concentrations measured in sampled cloud are also shown. Calcium data from Wardlow Hay Cop before 2000 are unreliable and have been omitted.

3.8 Trends in scavenging factors

The ratio of average hill cap-cloud concentration to rain concentration at the low-level site (assumed to be representative of the rain-bearing clouds) is used to model deposition, with a uniform ratio of 2 for all ions. This figure was based on the earlier campaign measurements of orographic enhancement at several sites in the UK. As can be seen from Figure 16, this value is not a good representation at this site for all ions; for nitrate, non-marine sulphate and calcium the value is closer to 1, as is also the case for ammonium if the anomalous value for 2003 is omitted. For sea salts the scavenging factor is larger, with an average of 3.6 for sodium. There have been no trends in the ratio throughout the period, but large variation from year to year.

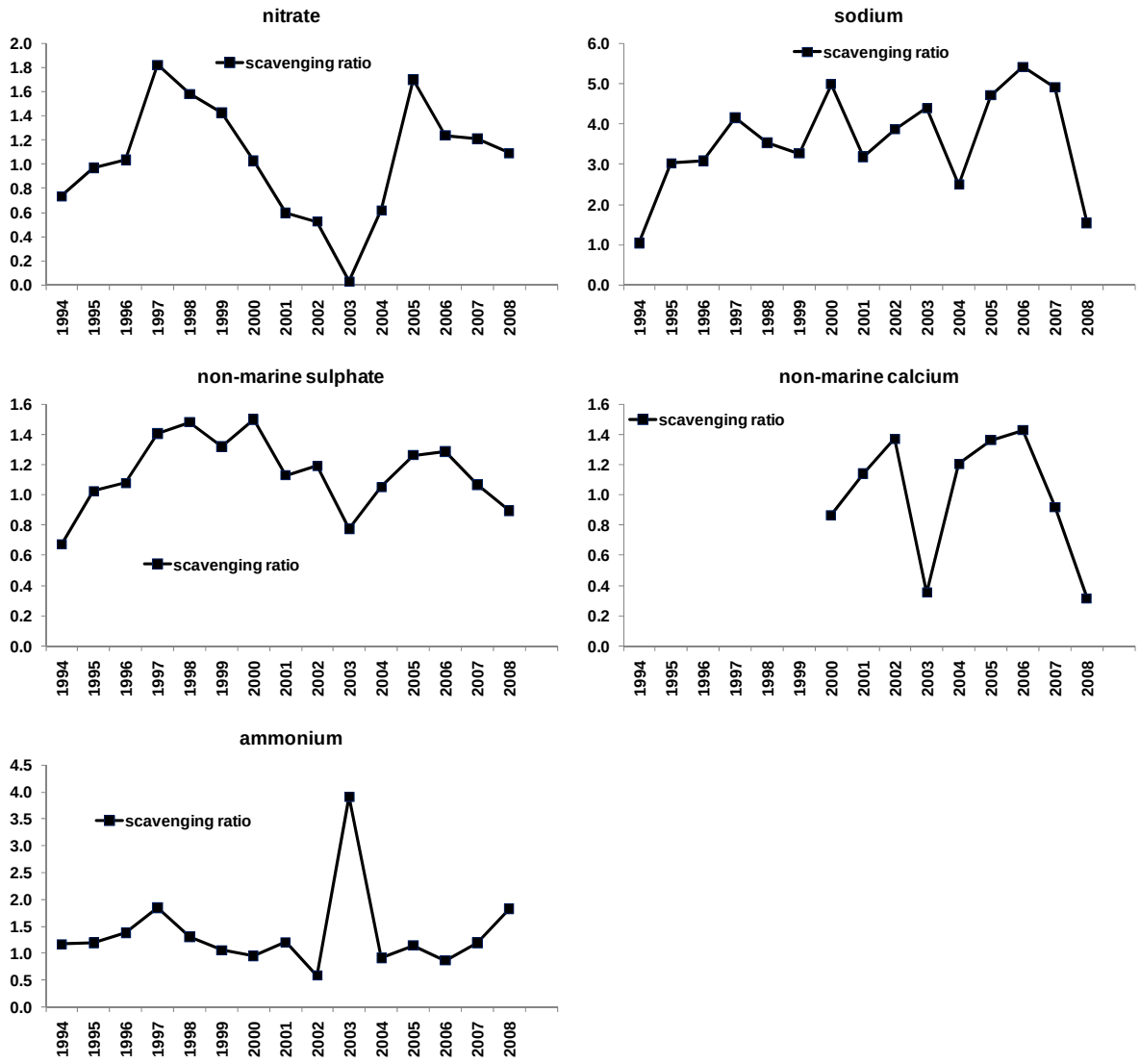

Figure 15. Time trend of scavenging factor, being the ratio of the cloud water concentration in scavenged cloud to the concentration in rain at Wardlow Hay Cop.

4. Interpretation

4.1 Trends in weather patterns

The changes in wind direction and wind speed noted in Section 3.3 suggest no over-riding temporal trend in weather patterns throughout the period, even though some characteristics appear to be significantly different between the early and late part of the study period. Perhaps the most obvious feature is the much greater year-to-year variability in rainfall amount at Holme Moss compared with Wardlow Hay Cop. This is directly related to the frequency, depth and water content of the hill cap cloud. Even here, no clear relationships emerge; the driest year in terms of rainfall (2003) gave higher-than-average capture of hill cloud at Holme Moss, implying greater frequency of occurrence, greater water content, higher wind speeds, or some combination of these three factors. The average amount of water-soluble material collected in cloud (Figure 12) was not remarkably greater that year, so the increased volume of cloud water sampled cannot have been simply caused by increased aerosol loadings in the upwind air. However, that year did show anomalous behaviour in

scavenging factors, particularly for ammonium and nitrate ions, with very low concentrations of nitrate, and high concentrations of ammonium, in the scavenged cloud (Figure 15).

4.2 Individual ions - nitrate

There was a weak downwards trend in nitrate concentrations in rain at both sites, but not in cloud concentration. There was a weak downward trend in wet deposition only at Wardlow Hay Cop. This observation contrasts with the ca.40% decrease in oxidised N emissions in the UK over the same period, but reflects the general pattern across the country of only small changes in nitrate concentrations in rainfall from 1994 to 2009 (RoTAP, 2010).

Perhaps more surprising is the rather small and highly variable values obtained for the scavenging factor, with values as small as zero in 2003. This observation suggests that some of the assumptions made in using a scavenging factor are not valid. In order for the simple seeder-feeder model to work, it has to be assumed that all the contributory ions are in the particle phase, and therefore are not scavenged efficiently by falling rain drops. However, for nitrate (and to a lesser extent for other ions) a significant proportion of the soluble nitrate may be in the gas phase, as nitric acid. Under such conditions, because of nitric acid's high solubility in water, falling rain upwind of the hill cap cloud would be expected to efficiently scavenge the gas-phase nitric acid, which would be deposited as nitrate at the 'low-level' site. The air mass would therefore be depleted of nitric acid before entering cloud and activation of the aerosol. Moreover, higher concentrations of gas-phase nitric acid at the lower elevation site would lead to enhanced deposition to the bulk collector used to sample rainfall, providing a positive bias in the amount of nitrate sampled (Gonzalez-Benitez et al., 2009).

The scavenging factor (as applied strictly to aerosol particles) would therefore be underestimated, because the low-level rain composition would have been enhanced by the solution of nitric acid, and the scavenged cloud deposition would have been depleted by removal of the nitric acid. Expressing this algebraically:

$$\text{Scavenging factor} = \frac{\text{(deposition at hill top – deposition upwind)}}{\text{(rain volume at hill top – rain volume upwind)}}$$

Deposition at the hill top

= (volume rain * rain concentration + volume scavenged cloud * cloud concentration)

= (volume rain * rain concentration + amount of aerosol scavenged)

Deposition upwind

= (volume rain * rain concentration + amount of gas scavenged)

If the amount of gas scavenged upwind is equal to the amount of aerosol scavenged in the cap cloud, then the scavenging factor is zero.

In this case, a scavenging factor of zero implies that there was approximately the same quantity of nitric acid in the gas phase upwind of the cloud as there was of nitrate aerosol. Normally, the balance between gas and aerosol phase is strongly in favour of the aerosol phase, with 'nitrate' existing mostly as ammonium nitrate. Under conditions of high temperature, the equilibrium is pushed towards the gas phase – possibly accounting for the rather low scavenging factor observed in 2003, despite the high scavenging factors for ammonium observed that year, implying that most of the ammonium was present as particles rather than as ammonia gas. Indeed, looking at the relative amounts of ammonium and other ions, in all years except 2003, and for both Holme Moss and Wardlow Hay Cop, the ratio of ammonium to the sum of nitrate and non-marine sulphate (as ion equivalents) was much less

than unity, with the ion balance largely made up by non-marine calcium. However in 2003 and in 2008 there was an excess of ammonium measured in rain at Holme Moss – presumably the ion balance was maintained by organic anions and/or bicarbonate. This also suggests that there may have been additional (local) sources of ammonia gas in these years at Holme Moss that did not influence rainfall composition at Wardlow Hay Cop.

4.3 Individual ions – non-marine sulphate

There was a significant decrease in non-marine sulphate in all the sampled rain and cloud at both sites, responding to the 90% reduction in UK emissions of sulphur dioxide over the period. As for nitrate, the scavenging factor occasionally falls below unity, implying a contribution from gas-phase sulphur dioxide, as for nitric acid in the case of nitrate. However, SO_2 is much less water-soluble than nitric acid, and so is less likely to be scavenged efficiently by falling rain, and less likely to affect the scavenging factor.

4.4 Individual ions – ammonium

There were no significant trends in ammonium concentration or deposition throughout the period, reflecting the relatively small change in UK emissions. The scavenging factor was around unity with the exception of 2003, as noted above, again suggesting possible gas-phase scavenging of ammonia by falling rain. Because of the widespread agricultural sources of ammonia, there is the greatest potential for a contribution at one site from sources that do not contribute to concentrations and deposition at the other, thereby invalidating the assumptions of the seeder-feeder modelling approach. As noted above, in general in rain and cloud, ammonium concentrations are less than those required to balance the sum of nitrate and non-marine sulphate.

4.5 Individual ions – sea salts

These ions, represented in the figures by sodium, have no gas-phase contributors and therefore act as ‘ideal’ tests of the seeder-feeder model. The scavenging factor is much higher than for the other ions, at an average of 3.6. No temporal trends were observed, although there was large year-to-year variation.

4.6 Individual ions – non-marine calcium

The source of non-marine calcium is presumably resuspended dust from agricultural or mining activity, and is likely therefore to be in the larger (super-micron) particle sizes. Also, as for ammonia, there may be localised sources that contribute differently to deposition at the two sites, making it difficult to match the assumptions necessary for operation of the seeder-feeder model. The average value of the scavenging factor is much smaller than that for sodium, and given that there are no gaseous sources of calcium it would appear that different local sources are contributing to the two sites, in contrast to the sodium ions, which come from long-range transport of sea-salt particles. From 2000 onwards, after the initial analytical problems with calcium concentrations at Wardlow Hay Cop, concentrations and deposition were fairly stable at Wardlow Hay Cop, but varied greatly at Holme Moss, implying varying amounts of input to the cap cloud between years, either from changes in wind direction and wind speed, or changes in activities leading to resuspension of calcium-containing particles.

5. Uncertainty analysis

The assumptions of the seeder-feeder model to estimate deposition of ions at high altitudes lead to uncertainty in the use of simple ratios for estimating direct deposition of cloud water, and the orographic enhancement of wet deposition. In order to put these uncertainties into context, the wet and dry deposition of different ions have been calculated for the years 2000 to 2008 inclusive, using a range of different values for the parameters used in estimating direct cloud deposition and orographic enhancement.

The simplest analysis is for sodium, which (as it is always in the particulate phase) conforms most closely to the seeder-feeder assumptions. The average scavenging factor at Holme Moss (Figure 15) is 3.6, somewhat greater than the default value of 2 used in the CBED model for all ions. Although we have no data on the spatial variation of this ratio for sodium across the UK, this difference in scavenging factor would make a 30% difference to annual wet-deposited sodium if it applied at all sites. For other ions, as seen in Figure 15, the measured scavenging factors at Holme Moss are smaller than those for sodium, reflecting deficiencies in the simple seeder-feeder model that ignore gas-phase constituents (section 4.2 above), so that a value for the scavenging factor for these ions which is smaller than that for sodium is likely to be more appropriate (i.e. 2 rather than 3.6).

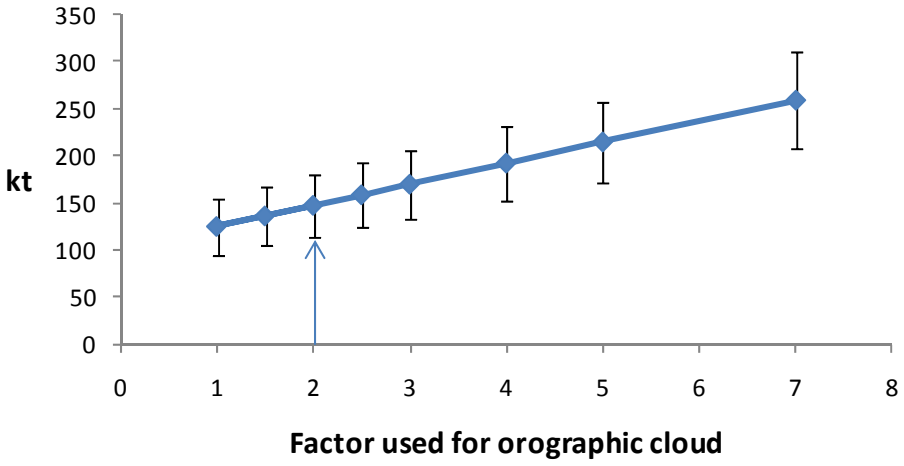

Figure 16. Average annual (wet+dry) deposition of S in the UK from 2000 to 2008 using different factors for the ratio of sulphate concentrations in scavenged cloud to the concentration in the low-elevation rainfall at a site. The default value in the current model is 2. The error bars show the year-to-year standard deviation.

Figure 16 shows the effect of changing the scavenging factor from the default value of 2 used across all of the UK. At Holme Moss the average scavenging factor is close to 1, suggesting that if that value is appropriate elsewhere, overall UK deposition of S may be overestimated by around 15% by the default parameter, which is well within the year-to-year variation in S deposition shown by the error bars in Figure 16.

Similarly, for total N deposition, Figure 17 shows that the use of an overall scavenging factor of 2 (the default) rather than 1 (as observed at Holme Moss) leads to an overestimate of annual N deposition to the UK of around 12%, also within the year-to-year uncertainty.

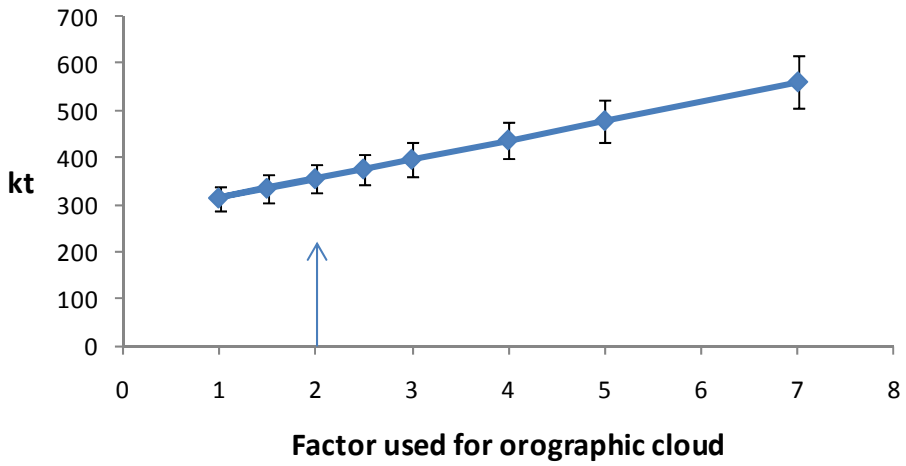

Figure 17. Average annual (wet+dry) deposition of N in the UK from 2000 to 2008 using different factors for the ratio of nitrate and ammonium concentrations in scavenged cloud to the concentration in the low-elevation rainfall at a site. The default value in the current model is 2. The error bars show the year-to-year standard deviation.

The effects of an uncertain value for the scavenging factor might be expected to be greater for those regions where N and S wet deposition is greatest, and in areas where Critical Loads are currently exceeded, or close to exceedance. The dependence of the N Critical Load exceedance on the scavenging factor is shown in Figures 18 and 19. In Figure 18, the effect of a change in scavenging factor on the exceedance of a 10 kg ha^{-1} y^{-1} Critical Load is shown as the change in number of grid squares where deposition exceeds the Critical Load. For the case of 10 kg N ha^{-1} y^{-1}, reducing the scavenging factor from 2 to 1 has the effect of reducing the number of grid squares in exceedance by 9%. For the case of 20 kg N ha^{-1} y^{-1}, the effect is much greater (60%) although the absolute number of grid squares involved is rather small. However, for the upland habitats where orographic enhancement is greatest, the empirical N Critical Load is likely to be 10 kg ha^{-1} y^{-1}.

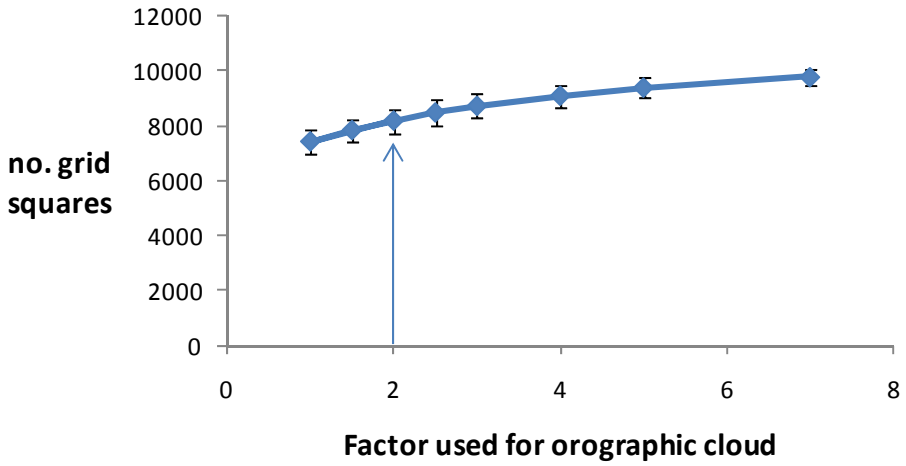

Figure 18. Number of grid squares in the UK for which the N Critical Load of 10 kg ha^{-1} y^{-1} is exceeded, in relationship to the scavenging factor used for calculating orographic enhancement at high elevations, for which the default is 2.

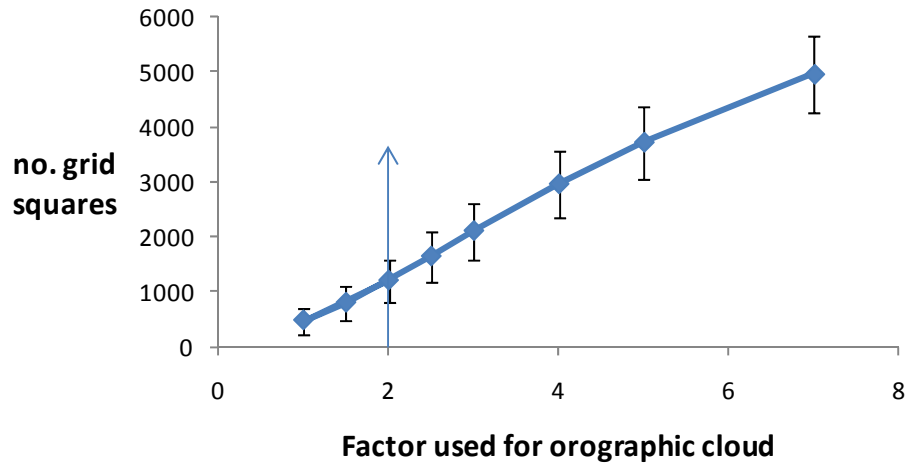

Figure 19. Number of grid squares in the UK for which the N Critical Load of 20 kg ha^{-1} y^{-1} is exceeded, in relationship to the scavenging factor used for calculating orographic enhancement at high elevations, for which the default is 2.

By contrast, the effect of changing the ratio of cloud concentration to rainfall (default 5), is minimal (<0.3% for a change from a factor of 5 to a factor of 1) both for UK deposition and for Critical Load exceedance, because the absolute deposition from this pathway is small.

6. Conclusions

Long-term monitoring of rain and cloud at Holme Moss since 1994 has shown strong downwards trends only in non-marine sulphate concentrations. Trends in ammonium and nitrate concentration are weakly downwards, despite the large decrease in NOx emissions in the UK over the period. This behaviour is similar to that seen in the UK rainfall network. There was no trend in sea-salt concentrations over the period, but there was large year-to-year variability, emphasising the need to collect data over many years before drawing conclusions over temporal trends.

Rainfall and cloud amounts showed no overall trend, although amounts were largest in the period 1998-2002. There was some evidence of a shift in wind direction at the site, with increasing wind speeds from the south-west; this shift in direction may have affected patterns of concentration and deposition, because of the varied sources of pollutant emissions around Holme Moss. This makes the interpretation of temporal trends in concentration and deposition more difficult, especially with the use of time-integrated (two-weekly) sampling, which combines rainfall events from different types of weather system and wind directions.

The main purpose of the long-term monitoring of rain and cloud was to confirm the lack of any long-term trend in the parameters used to estimate direct cloud deposition and orographic enhancement of wet deposition over the UK. For direct cloud deposition, a default factor of 5 is used to estimate cloud water concentrations relative to predicted low-elevation rain concentrations at a site. Although year-to-year variation is substantial, the data from Holme Moss show no evidence of either a temporal trend, or a need to change the default factor. Although direct cloud deposition may be locally important, it makes a very small contribution to the UK budget, and even to estimates of Critical Load exceedance. Any uncertainty in the default factor of 5 used in deposition estimates is therefore negligible.

For orographic enhancement, the seeder-feeder model assumes that enhancement of hill cap cloud concentrations arises from the activation and capture of particulate material in cloud droplets that is

not removed from the atmosphere by falling rain upwind of the hill. This assumption is only met for material which exists only in the aerosol phase, such as sea-salts. At Holme Moss the average 'scavenging factor' for sodium, i.e. the ratio of the concentration of sodium in scavenged cloud to that in rainfall at the nearby 'low-level' site of Wardlow Hay Cop, was 3.6, which is approximately twice the default value of 2 used for all ions for calculating orographic enhancement across the UK. This means that the current model underestimates seeder-feeder enhancement of sea salts at this site, and presumably also over the UK as a whole.

For pollutant-derived ions (sulphate, nitrate and ammonium) the assumptions of the seeder-feeder model are not met in that some contribution from gas-phase species is to be expected. If the gas-phase is not efficiently scavenged by falling rain then the effect on the seeder-feeder calculation will be small, provided that there is no significant difference between gas-phase concentrations at low and high-level sites. However, if there is a gas-phase contribution to solutes at the low-level site, and systematically lower concentration in the gas-phase at the elevated site, the scavenging factor will be smaller than that observed for sea-salts. This is clearly demonstrated in the data from Holme Moss, with the scavenging factors for non-sea sulphate, nitrate and ammonium close to 1, rather than the default value of 2.

In terms of potential bias in calculating UK budgets and Critical Load exceedances this difference of a factor of 2 between the measurements and the model contributes a relatively small uncertainty, well within the year-to-year variability. However, this remains an uncertainty for the current model, because the scavenging factor is only measured at one site. Moreover, the location of Holme Moss, close to some of the higher concentrations of gas-phase pollution in the UK, suggests that the contribution from gas-phase species is probably much greater here than at sites in the north-west of Scotland, north Wales and the Lake District where orographic enhancement is important. Consequently, the default factor of 2 used for the scavenging factor may not be too far from the actual value over much of the northern and western uplands of the UK.

The long-term data allow us to generalise about processes operating at the site without too much emphasis on the year-to-year variability. Consequently, the problems with the seeder-feeder assumptions can be investigated. The deviation caused by the presence of gas-phase species is seen to dominate the value of the scavenging factor. However, the influence of gas-phase species can be estimated if the gas-phase concentrations at upper and lower sites can be measured, by including the appropriate correction factors in the seeder-feeder equations. Improvements in the estimates, and reductions in uncertainty, could therefore be achieved by measuring these concentrations rather than by interpolating them from the (low-level) measurement sites in the UKEAP network.

7. Options for the future

Several options exist for future measurements of cloud and high-elevation rainfall in the UK.

1. ***Cease all monitoring at Holme Moss***
   Pro: cost saving of ca. £30k p.a.
   Con: loss of long-term monitoring from the only high-elevation site in the UK and the ability to verify whether the scavenging factor used in estimating seeder-feeder deposition is appropriate. Need to provide site operating costs for heavy metals monitoring network sampling at Holme Moss, currently covered by the APDP contract.
   Cost implications: ca. £10k p.a.

2. ***Continue as is***
   Pro: maintains the integrity of long-term monitoring at Holme Moss, and provides logistical support for heavy metals monitoring at the site. Measurements at high and low elevation nearby continue to provide effective scavenging factors for estimating

the validity of the factor(s) used in calculating seeder-feeder enhancement of deposition across the UK.
Con: cloud water monitoring provides little additional information for deposition modelling, given the lack of any temporal trend in the ratio between cloud and rain concentrations, and the small contribution made by direct deposition of cloud water even to upland sites. Scavenging factors only available for this one site, and may not be appropriate for other regions of the UK.
Cost implications: ca. £40k p.a.

3. ***Monitor rain only at HM***
   Pro: maintains the integrity of long-term monitoring at Holme Moss, and provides logistical support for heavy metals monitoring at the site. Measurements at high and low elevation nearby continue to provide effective scavenging factors for estimating the validity of the factor(s) used in calculating seeder-feeder enhancement of deposition across the UK. Lower analytical costs than option 1 (no cloud analysis)
   Con: scavenging factors only available for this one site, and may not be appropriate for other regions of the UK.
   Cost implications: ca. £25k p.a.

4. ***Monitor rain only at several high/low site pairs in different parts of the UK (e.g. east)***
   Pro: provides independent estimates of the scavenging factor for seeder-feeder enhancement in different regions of the UK where gas and aerosol concentrations may be different from Holme Moss, thereby reducing uncertainty cf. option 2.
   Con: additional cost of sampling and chemical analysis. Need to identify suitable paired high and low-level sites, which might mean moving or adding to sites in the current UKEAP network, or using other sites (e.g. ECN).
   Cost implications: ca. £25k + est. £5k per site (installation) + £2k per site p.a. (analysis)

5. ***In addition to option 4 above, install conditional Delta denuder samplers at paired high and low elevation sites*** to measure air concentrations of gaseous and particulate species so that 'corrected' scavenging factors can be calculated. 'Conditional' denuder samplers only sample in the absence of cloud water – this implies a requirement for some means of determining the presence of cloud and/or rain water, which could be achieved through use of a wetness sensor.
   Pro: reduces uncertainty in seeder-feeder calculations. Improves data for trace gas and particle concentrations at high elevations, and permits better estimates of dry deposition at high elevations (current methods assume no altitude dependence of gas and particle concentrations when interpolating between AGAP sites).
   Con: additional costs for preparation and analysis of denuder and filter samples, and initial costs of Delta systems and power supplies.
   Cost implications: additional £5k per site (installation) + £2k per site (analysis)

8. Recommendations

The current position (cloud and rain monitoring at Holme Moss only) provides verification at a single site of the scavenging factor used in the estimation of deposition at high elevations based on the seeder-feeder model, and is adequate to detect any long-term changes. Cloud composition monitoring could be stopped with little detrimental effect on modelling wet

deposition to the UK. However, the main source of uncertainty is the application of the seeder-feeder model across the UK using data from only one site.

Consequently, we recommend:

(i) the adoption of option 4 at a minimum of 2 additional paired sites representative of regions where seeder-feeder enhancement is an important contributor to Critical Load exceedance for N deposition.

The other main source of uncertainty is the role of gas-phase scavenging as it affects the underlying assumptions of the seeder-feeder model. This is linked to the uncertainty in estimating trace gas concentrations across the UK from the denuder/filter samplers in AGANET, particularly at high elevations, where data are sparse and where dry deposition contributes significantly to total deposition. We therefore also recommend:

(ii) the adoption of option 5 at a minimum of 2 sites (Wardlow Hay Cop and Holme Moss), and ideally at the other locations where paired high- and low-level rain samplers are installed under option 4.

Although a costlier process than the current position, a period of short-term (3-5 year) monitoring under options 4 and 5 would greatly improve the current uncertainties in deposition across the UK, and in estimating Critical Load exceedance at high elevations.

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